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# The Synthesis of Spiro[adamantane-[1,2]dioxetanes]

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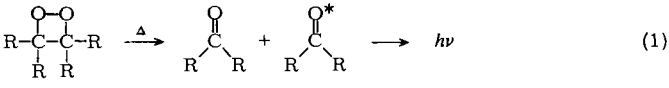
It is shown that the spiroadamantane group stabilizes thermally labile 1,2-dioxetanes sufficiently to permit isolation. With the help of this stabilizing group it was possible to prepare the first sulfur substituted dioxetanes **9k** and **l** and characterize them by low temperature $^{13}C$ and $^{1}H$ NMR spectra. Photosensitized singlet oxygenation at low temperature, using either polymer-bound Rose Bengal or tetraphenylporphyrin as sensitizer in methylene chloride, of the corresponding 2-methyleneadamantanes **8** was the method of choice for the preparation of the spiro[adamantane-[1,2]dioxetanes] **9**, provided that the methylene carbon bears no alkyl or phenyl substituents. The *Kopecky* method, i.e. hydroperoxybromination of the 2-methyleneadamantanes **8** and subsequent dehydrobromination, proved unsuccessful to prepare the dioxetanes **9**.

**Die Synthese von Spiro[adamantan-[1,2]dioxetanen]**

Die Spiroadamantangruppe stabilisiert thermisch unbeständige 1,2-Dioxetane ausreichend und ermöglicht dadurch deren Isolierung. Diese stabilisierende Gruppe erlaubt erstmals, schwefelsubstituierte Dioxetane **9k** und **l** herzustellen und mittels $^{13}C$- und $^{1}H$-NMR-Spektroskopie nachzuweisen. Tetraphenylporphyrin-photosensibilisierte Singulett-Sauerstoff-Cycloaddition an 2-Methylenadamantane **8** ist die Methode der Wahl zur Erzeugung der Spiro[adamantan-[1,2]-dioxetane] **9**, vorausgesetzt, der Methylenkohlenstoff trägt keine Alkyl- oder Arylreste. Die *Kopecky*-Methode, d.h. Hydroperoxybromierung der 2-Methylenadamantane **8** und anschließende Dehydrobromierung, führt nicht zur Bildung der Dioxetane **9**.

1,2-Dioxetanes **1** are thermally labile substances which decompose on heating with light emission[1]. Consequently these "high-energy" molecules store sufficient energy to generate on fragmentation electronically excited carbonyl products which are responsible for the observed chemiluminescence (Eq. 1)[2]. The wide range in thermal stability of these intriguing compounds is impressive. For example, among the least stable figures the spiroacridan derivative **2**[3], while the most stable derivative is the dispiroadamantane system **4**[4]; the mixed system **3**[5] is intermediate in stability. Thus, although **2** – **4** are all spiro-substituted 1,2-dioxetanes, spiroadamantane substitution exerts a tremendous stabilizing effect on these four-membered ring peroxides. For example, single spiroadamantane substitution as in **3** stabilizes the dioxetane sufficiently to permit isolation and purification[4], which was not possible for **2**[3].




**1** (1)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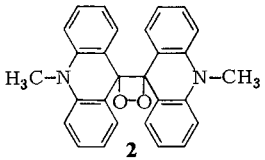
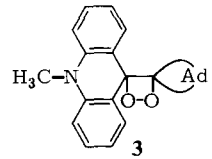


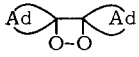
**2**

$E_a \approx 18$



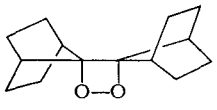
**3**

≈ 26

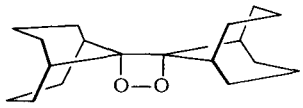


**4**

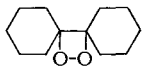
≈ 35 kcal/mol



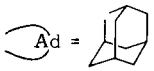
**5**



**6**



**7**



(Spiro bonding)

The reasons for the stabilizing nature of the spiroadamantane group are not clear; but the stabilizing effect of bulky and rigid spiro substituents seems to be general, as confirmed by the dioxetanes **5**[6] and **6**[7] in contrast to **7**[8]. Again, **5** – **7** are all spiro-substituted, but **5** and **6** possess caged structures like diadamantylidenedioxetane **4** and are considerably more stable than **7**.

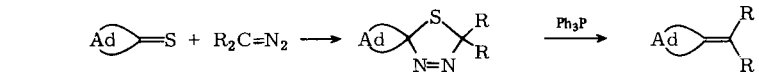
Whatever the causes of the stabilizing nature of spiroadamantane substitution are, it should be of utility in the synthesis of stable dioxetanes that might be of interest for mechanistic investigations. Consequently, we have undertaken the preparation of a series of spiroadamantane-substituted dioxetanes **9** from the corresponding olefins **8** (Eq. 2) and report herein the results of our synthetic efforts.

(2)

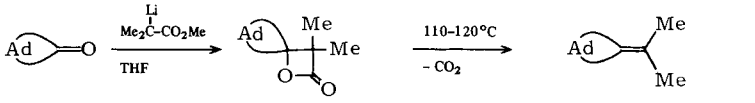
| | a | b | c | d | e | f | g | h | i | j | k | l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | H | Ph |  | $CH_3$ | H | H | H | OPh | $OCH_2Ph$ | H | H |  |
| X' | H | Ph |  | $CH_3$ | OPh | $OC_6H_4$ -*p*-Br | $OCH_2Ph$ | OPh | $OCH_2Ph$ |  | SPh | |

## Preparation of Olefins 8

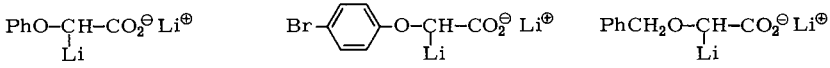
Methyleneadamantane (**8a**) was prepared in 76% yield via Wittig reaction of methylenetriphenylphosphorane with adamantanone[9]. For the synthesis of benzhydrylidene- and fluorenylideneadamantanes (**8b** and **c**) we employed the convenient sulfur extrusion route[10] shown in Eq. (3). In this way olefins **8b** and **c** could be obtained in 55 and 15% yields, respectively. It is particularly significant to point out that the respective β-lactone routes[11] were unsuccessful because the enolates of fluorenylidenecarboxylic acid and diphenylacetic acid did not react with adamantanone to give the required β-hydroxy acids for β-lactonization.



(3)



(4)

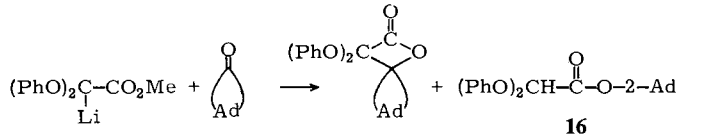


**10a** **10b** **11**

The β-lactone method[11] (Eq. 4) was the most convenient route to prepare isopropylideneadamantane (**8d**). Using methyl α-lithioisobutyrate as enolate instead of lithium α-lithiobutyrate, the β-lactone (Eq. 4) was obtained directly in 85% yield, without requiring isolation and subsequent cyclization of the corresponding β-hydroxy acid. On heating at 110 – 120 °C the pure olefin **8d** was obtained in 95% yield. Similarly, the β-lactone route was used to prepare (phenoxymethylene)-, (4-bromophenoxymethylene)-, and (benzyloxymethylene)adamantanes (**8e, f, g**) in 76, 80, and 92% yields, resp., by employing the enolates **10a**[12], **10b**, and **11**[13] as synthons. Here it is of interest to mention that the condensation of the corresponding methyl ester enolates of **10a** and **b** with adamantanone did not lead directly to the β-lactones as was the case with methyl α-lithioisobutyrate (Eq. 4). Apparently *gem*-substitution at the α-carbon is essential for cyclization.

The syntheses of the (diphenoxymethylene)- and (dibenzyloxymethylene)adamantanes (**8h, i**) were problematic. As previously reported[14], the use of the enolate synthon lithium α-lithiodiphenoxyacetate (**12**) gave with adamantanone the rearranged keto-

**12** **13**



(5)

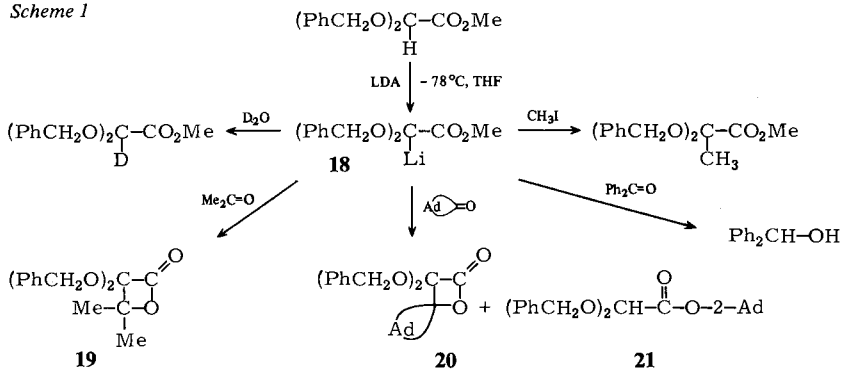
**14** **15** **16** 2-Ad = 2-Adamantyl

**17** **18**

ester **13** after treatment with diazomethane. However, utilization of the methyl α-lithiodiphenoxyacetate (**14**) as enolate gave like methyl α-lithioisobutyrate (Eq. 4) the desired β-lactone, but only in 6% yield (Eq. 5). The major product (ca. 14% yield) was 2-adamantyl diphenoxyacetate (**16**), showing the complexity of this reaction. It is known[15] that lithium diisopropylamide (LDA), which is used for the preparation of the ester enolate **12**, can act as Meerwein-Ponndorf-Verley reductant of sterically hindered ketones. Presumably the 2-adamantyloxy anion is formed in this way, which undergoes transesterification with methyl diphenoxyacetate to afford ester **16** and 2-adamantanol after hydrolysis. In any case, sufficient β-lactone **13** could be obtained to decarboxylate it into the desired olefin **8h** in 89% yield.

Our experiences with the enolates **17** and **18**, which are derived via α-lithiation from dibenzyloxyacetic acid and methyl dibenzyloxyacetate, resp., as synthons for the preparation of (dibenzyloxymethylene)adamantane (**8i**), were still more discouraging. Enolate **17** could not be obtained using LDA at −78 °C in THF with or without hexamethylphosphoric triamide (HMPA) or directly with butyllithium. This was evidenced by the failure of the resulting reaction mixture to undergo α-deuteration with $D_2O$, α-methylation with methyl iodide, or reaction with ketones. After hydrolysis, benzyl alcohol and benzaldehyde were isolated, indicating that lithiation took place at the benzylic position of the benzyloxy substituent.

*Scheme 1*

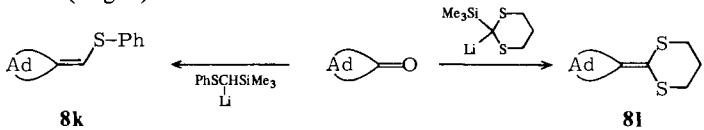



On the other hand, the ester **18** could be generated essentially quantitatively via α-lithiation of methyl dibenzyloxyacetate with LDA in THF at −78 °C, as confirmed by α-deuteration with $D_2O$ and α-methylation with methyl iodide (Scheme 1). Of the ketone electrophiles only acetone gave a good yield (50%) of the corresponding β-hydroxy ester, which on saponification and subsequent treatment with benzenesulfonyl chloride in pyridine resulted in the desired β-lactone (37% yield), i.e. 3,3-dibenzyloxy-4,4-dimethyl-2-oxetanone (**19**). With adamantanone a 3.5% yield of the spiro-[adamantan-oxetan]-4′-one **20** and an 18% yield of 2-adamantyl dibenzyloxyacetate (**21**) were obtained. However, at −78 °C and 2 h reaction time, followed by immediate work-up, the β-lactone **20** could be isolated in 25 % yield. Again, Meerwein-Ponndorf-Verley-type reduction of adamantanone by the excess LDA must have taken place, analogous to the results for the ester enolate **13** (Eq. (5).

For benzophenone this reduction was the exclusive path leading to benzhydrol. Attempts to decarboxylate the β-lactones **19** and **20** to the corresponding olefins either thermally or treating with silica gel led to benzyloxyisobutyrate and 2-adamantanecarboxylate, respectively. Apparently (dibenzyloxymethylene)adamantane (**8i**) is formed, but this reactive ketene acetal does not survive and is hydrolyzed readily to the corresponding ester. Thus, it was not possible to prepare olefin **8i** via this route.

(Morpholinomethylene)adamantane (**8j**) was obtained in 85% yield via *p*-toluenesulfonic acid-catalyzed condensation of 2-adamantanecarboxaldehyde with an excess of morpholine, azeotroping off the water of dehydration with benzene. The previously unknown enamine **8j** was characterized on the basis of its infrared and $^1H$ and $^{13}C$ NMR spectra. Characteristic was the olefinic proton as a singlet at 5.1 ppm, the olefinic carbon as a doublet at 128.3 ppm and a corresponding C=C–N vibration at 1670 $cm^{-1}$.

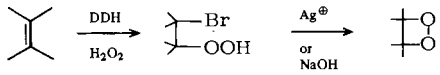
The sulfur-substituted methyleneadamantanes **8k** and **l** (62 and 66%, resp.) were prepared from adamantanone using, respectively, the α-lithio-α-(trimethylsilyl)thioanisole[16,17] and 2-lithio-2-(trimethylsilyl)-1,3-dithiane[18] as synthons (Eq. 6). Their physical constants and spectral data matched the reported ones. In addition, we give the $^{13}C$ NMR spectra of these thioenol ethers (cf. Experimental Part). Here it is of interest to mention that the methylene carbon in **8k** resonates at δ = 106.5 (doublet) and in **8l** at δ = 102 (singlet).




**8k** **8l** (6)

## Preparation of Dioxetanes 9

Two methods are available for the preparation of 1,2-dioxetanes, namely singlet oxygenation[19] and dehydrohalogenation (*Kopecky* route, Eq. 7)[20]. These methods are usually complementary and both have their advantages and difficulties. Of the two, photosensitized singlet oxygenation is the prefered in view of its convenience and higher yields. Thus, using tetraphenylporphyrin (TPP) or polymer-bound Rose Bengal (P-RB) as sensitizers at 0 or −20 °C in $CCl_4$ or $CH_2Cl_2$, respectively, and a 150-W high pressure sodium vapor lamp as light source[21], the 1,2-dioxetanes **9c**, **e**–**g** and **h**, derived from fluorenylideneadamantane (**8c**), the enol ethers **8e**–**g**, and the ketene acetal **8h**, were readily obtained as stable, yellow, crystalline solids.



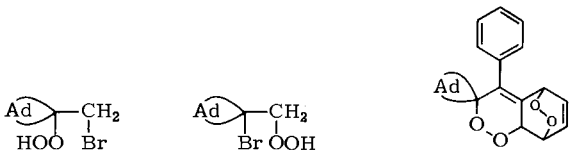

(7)

Singlet oxygenation of the enamine **8j** and the thioenol ethers **8k** and **l** at ca. 0 °C gave the expected dioxetane cleavage products, i.e. adamantanone and *N*-formylmorpholine, *S*-phenyl thioformate, and 1,3-dithian-2-one, respectively, as confirmed by the appropriate C=O frequencies in the infrared. It was, therefore, attempted to run the singlet oxygenations at −78 °C and monitor the dioxetane formation by low temperature NMR. For this purpose we employed $^{13}C$ NMR because of the characteristic dioxetane carbon resonances at ca. 90–100 ppm.

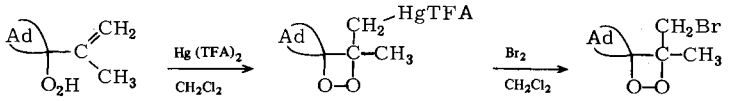
Even at −78 °C it was not possible to observe the intermediary dioxetane **9j** with $^{13}C$ NMR in the singlet oxygenation of the enamine **8j**. Only the characteristic carbonyl carbon resonances of the fragmentation products were detected. However, the low temperature $^{13}C$ NMR experiments were successful and definitive for the characterization of the novel sulfur-substituted dioxetanes **9k** and **l**. At −63 °C the dioxetane **9k** showed the dioxetane ring carbons at 93.1 (singlet, spiroadamantane) and 100.2 ppm (doublet, sulfur-substituted), respectively, which on warming to room temperature disappeared due to thermal decomposition of the dioxetane. Similarly, at −50 °C the dioxetane **9l** exhibited the dioxetane ring carbons at 96.6 ppm (singlet, spiroadamantane) and 109.6 (singlet, sulfur-substituted), which also disappeared on warming. Unfortunately it was not possible to isolate these thermally labile dioxetanes by column chromatography on Florisil at −78 °C. Only fragmentation products of these dioxetanes were isolated, as confirmed by their characteristic C=O frequencies in the infrared. However, both dioxetanes **9k** and **l** showed weak chemiluminescence.

It is important to point out that the labile dioxetanes **9k** and **l** are the first characterized sulfur-substituted derivatives of this class of "high energy" molecules[1]. In fact, in our report[22] we postulated dioxetane **9l** as an intermediate, but were not equipped to provide spectral evidence for it.

With the remaining olefins **8a,b,d** serious difficulties were encountered on attempted singlet oxygenation. For example, methyleneadamantane (**8a**) was completely inert towards singlet oxygen even after 85 h of continuous irradiation with a 250 W Na-lamp in an immersion photolysis apparatus. Attempts to prepare the dioxetane **9a** via the *Kopecky* route[20] did not lead to the expected bromohydroperoxide **22a,b**. Although it was impossible to characterize the complex reaction mixture, it appears that skeletal rearrangement of the adamantane moiety had taken place.




**22a** **22b** **23**




**24** **25** **26** (8)

Benzhydrylideneadamantane (**8b**) with singlet oxygen gave exclusively the [4 + 2]-cycloadduct **23**. Although this reaction is well documented for electron-rich arylalkenes[23], it is surprising that the sterically congested olefin **8b** can align the phenyl ring with the exocyclic double bond for [4 + 2]-cycloaddition. The characterization of the endoperoxide **23** rests on correct elemental composition and spectral data (cf. Experimental Part). Attempts to rearrange **23** into its dioxetane **9b** either thermally or

with silica gel failed[24]. However, it is of interest to mention that appreciable direct chemiluminescence could be observed during these transformations. Apparently the expected 1,2-dioxetane **9b** is formed, but does not accumulate. Efforts to prepare **9b** via the *Kopecky* route (Eq. 7)[20] were unsuccessful already in the hydroperoxybromination step because **8b** was completely inert to 1,3-dibromo-5,5-dimethylhydantoin (DDH) and hydrogen peroxide.

In the case of isopropylideneadamantane (**8d**), singlet oxygenation led exclusively to the allylic hydroperoxide **24** (Eq. 8). Although singlet oxygenation proved unsuccessful for the preparation of dioxetane **9d**, via intramolecular peroxymercuration with mercury trifluoroacetate and subsequent bromination[25] the bromodioxetane **26** could be obtained (cf. Experimental Part). Attempts to convert the mercuriated dioxetane **25** with sodium borohydride to the desired dioxetane **9d** led to reduced ring-opened products. Also the *Kopecky* route with olefin **8d** failed. Again difficulties were encountered already in the hydroperoxybromination step (Eq. 7) with 1,3-dibromo-5,5-dimethylhydantoin (DDH), which led mainly to allylic bromination of **8d**. The minor peroxidic product showed unsaturated functionalities, as evidenced by $^1$H NMR and infrared. The complex product mixture was, nevertheless, submitted to base- and silver ion-catalyzed dehydrobromination (Eq. 7), but no desired dioxetane product **9d** could be detected.

We are grateful to the *Deutsche Forschungsgemeinschaft,* the *Fonds der Chemischen Industrie,* the *National Institutes of Health,* the *National Science Foundation,* and the *Petroleum Research Fund,* administered by the *American Chemical Society,* for financial support of this work. L. A. thanks the *Alexander von Humboldt-Stiftung* for a travel grant. The assistance of Dr. *D. Scheutzow* in measuring and interpreting the $^{13}$C NMR spectra is especially appreciated. Prof. *G. Maier* (University of Giessen) was kind enough to run many of the elemental analyses for us and we are much indebted to him for this help.

## Experimental Part

Boiling and melting points are uncorrected. – Infrared spectra: Beckman Acculab. – $^1$H NMR spectra: Varian T-60, Hitachi-Perkin-Elmer R-24B, or 90 MHz Bruker HFX 10. – $^{13}$C NMR: Bruker WM 400. – Elemental analyses: Performed in house or run for us by Prof. *G. Maier*'s staff (University Giessen). – Commercial reagents and solvents were purified according to literature procedures to match reported physical and spectral data. Known compounds used in this research were either purchased or prepared according to literature procedures and purified. – Photooxygenations: 150 W sodium street lamp.

1. *Fluorenylideneadamantane* (**8c**): A solution of adamantanethione[26] (4.0 g, 24.1 mmol) and diazafluorene[27] (3.96 g, 20.6 mmol) in 100 ml of dry THF were refluxed under $N_2$ for 4 h. After roto-evaporation of the solvent (25 °C/18 Torr), the residue was submitted to silica gel chromatography at 25 °C, eluting with petroleum ether (30 – 50 °C). The crude product was dissolved immediately in 100 ml of dry THF and refluxed together with triphenylphosphane (6.05 g, 34 mmol) for 19 h. The solvent was removed by roto-evaporation (25 °C/18 Torr). The residue was stirred for 3 h at 25 °C with excess methyl iodide (5 ml) in petroleum ether (30 – 50 °C) (80 ml), the phosphonium salt removed by filtration, and the solid washed with more petroleum ether. The combined filtrates were concentrated and submitted to silica gel chromatography (1 : 10 ratio

of substrate to adsorbant) at 25 °C, eluting with petroleum ether. Subsequent recrystallization from hot ethanol/acetone gave the pure olefin **8c** in 15% yield (0.85 g), m.p. 232–234 °C. – IR ($CH_2Cl_2$): 3060, 3020, 2910, 2855, 1615, 1600, 1445, 1340, 960 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$): δ = 1.9–2.3 (m, 12H), 3.95 (broad s, 2H), 7.0–7.2 (m, 4H), 7.4–7.8 (m, 4H). – $^{13}C$-NMR ($CDCl_3$): δ = 27.6, 28.3, 35.6, 36.3, 36.5, 37.0, 37.7, 38.9, 39.6, 40.3, 118.8, 120, 123.8, 123.9, 125.1, 126.1, 126.9, 127.3, 139.4, 139.9, 159.9.

$C_{23}H_{22}$ (298.4) Calcd. C 92.57 H 7.43 Found C 92.59 H 7.43

2. *Benzhydrylideneadamantane* (**8b**) was prepared in 55% yield, starting from adamantanethione[26], according to the procedure of *Bartlett*[19], m.p. 109–110 °C, granular crystals from hexane (lit.[28] 107–109 °C).

3. *3',3'-Dimethylspiro[adamantane-2,2'-oxetan]-4'-one:* To a cold solution of LDA (2.46 g, 23.0 mmol) in 50 ml of dry THF kept under nitrogen at –78 °C was added a solution of methyl isobutyrate (1.81 g, 17.7 mmol) in dry THF (8 ml) by means of a syringe. The enolate solution was stirred for 35 min and a solution of adamantanone (2.7 g, 18 mmol) in THF (15 ml) was added. The mixture was stirred at –78 °C for 4 h. After roto-evaporation of the solvent (20 °C/18 Torr), the residue was dissolved in ethyl ether (50 ml) and washed with water (50 ml). The aqueous layer was extracted with ether (2 × 30 ml). The combined ether extracts were dried over $MgSO_4$ and roto-evaporated (25 °C/18 Torr). The residue was submitted to silica gel chromatography (1 : 20 ratio of substrate to adsorbant) at 25 °C, eluting with hexane/ether (4 : 1), resulting in 3.37 g (85%) of the β-lactone, m.p. 110.5–112 °C (colorless needles from hexane). – IR ($CCl_4$): 2990, 2910, 2860, 1830, 1450, 1385, 1380 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.34 (s, 6H), 1.58–2.1 (m, 12H), 2.2 (broad s, 2H).

$C_{14}H_{20}O_2$ (220.3) Calcd. C 76.32 H 9.15 Found C 76.27 H 9.18

4. *Isopropylideneadamantane* (**8d**): 2.01 g (9.15 mmol) of the above β-lactone was heated at 110–120 °C until cessation of $CO_2$ evolution. The residue was submitted to silica gel chromatography (1 : 10 ratio of substrate to adsorbant) at 25 °C, eluting with hexane, which gave 1.53 g (95%) of pure olefin **8d**, m.p. 43–44 °C (needles from pentane; lit.[29] b.p. 104–105 °C/9 Torr. – IR ($CCl_4$): 2980, 2920, 2880, 1465, 1450, 1370, 1100 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.6 (s, 6H), 1.6–2.1 (m, 12H), 2.85 (broad s, 2H).

5. *(4-Bromophenoxy)acetic acid:* A solution of phenoxyacetic acid (5.0 g, 32.88 mmol) and bromine (3 ml) in $CCl_4$ (200 ml) was refluxed for 12 h. The solvent was removed by distillation (74–76 °C/760 Torr) and the residue was dissolved in ether (80 ml), washed with water (3 × 20 ml), and dried over $MgSO_4$. Roto-evaporation of the solvent (25 °C/5–10 Torr) and recrystallization from hexane/ether (1 : 2) gave 3.9 g (50%) of the acid, m.p. 156–158.5 °C, needles from hexane/ether (3 : 1) (lit.[30] m.p. 157 °C). – IR ($CHCl_3$): 3690, 3620, 3020, 1740, 1490, 1425, 1200, 1070, 930, 750 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$): δ = 4.6 (s, 2H), 7.0 (AA'BB' pattern, 4H, $C_6H_4$), 7.8 (s, 1H).

6. *Lithium α-lithio-(4-bromophenoxy)acetate* (**10b**): LDA (1.04 g, 9.69 mmol) in dry THF (20 ml) were cooled to –78 °C and under nitrogen (4-bromophenoxy)acetic acid (0.559 g, 2.42 mmol) in dry THF (5 ml) was added by means of a syringe. The mixture was stirred at –78 °C for 30 min, resulting in the yellow solution of enolate **10b**.

7. *α-(4-Bromophenoxy)-2-hydroxy-2-adamantaneacetic acid:* To the above prepared enolate solution was added at –78 °C adamantanone (0.726 g, 4.84 mmol), dissolved in dry THF (5 ml). The mixture was stirred at –78 °C for 3 h and for 1 h at 26 °C. After roto-evaporation of the solvent (25 °C/10–20 Torr), the residue was dissolved in 30 ml of water and extracted with ether (2 × 20 ml). The aqueous phase was cooled to 0–10 °C, acidified with 20% HCl, and extracted

with ether (3 × 20 ml). The ether extracts were dried over $MgSO_4$ and roto-evaporated (25 °C/10 – 20 Torr). The residue was recrystallized from methylene chloride/ether giving 0.513 g (59%) of pure β-hydroxy acid, m.p. 121 – 124 °C. – IR (KBr): 3400, 2910, 2890, 1700, 1600, 1500, 1225, 1170, 1140, 1050, 1005, 890, 820, 720, 695 $cm^{-1}$. – $^1H$ NMR ($CD_3COCD_3$): δ = 1.6 – 2.5 (m, 14H), 4.5 (broad s, 2H), 5.15 (s, 1H), 7.1 (AA'BB' pattern, 4H, $C_6H_4$).

$C_{18}H_{21}BrO_4$ (381.1) Calcd. C 56.68 H 5.55 Br 20.97 Found C 56.88 H 5.62 Br 21.05

8. *[(4-Bromophenoxy)methylene]adamantane* (**8f**): A solution of 1.05 g (2.75 mmol) of the above β-hydroxy acid in 4.0 ml of dry pyridine was cooled to 0 °C and benzenesulfonyl chloride (2.768 g, 15.7 mmol) was added dropwise under nitrogen. The mixture was stirred until the formation of a precipitate (20 – 40 min) and stored overnight in the refrigerator (ca. 5 °C). The reaction mixture was poured onto 30 ml of ice-water and extracted with ether (4 × 40 ml). The combined ether extracts were washed with saturated $NaHCO_3$ solution (3 × 25 ml) and with water (4 × 30 ml). After roto-evaporation of the solvent (25 °C/10 – 20 Torr), the residue was dissolved in 20 ml $CCl_4$ and stirred with 10 g silica gel for 30 min. The silica gel was removed by filtration, the filtrate concentrated and the residue submitted to silica gel chromatography (1 : 10 ratio of substrate to adsorbant) at 25 °C, eluting with hexane. Yield 0.698 g (80%), m.p. 62.5 – 64.5 °C (plates from hexane). – IR ($CCl_4$): 3080, 3040, 2910, 2850, 1685, 1590, 1485, 1450, 1380, 1300, 1240, 1155, 1100, 1060, 1000, 830, 710 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.6 – 2.1 (m, 12H), 2.3 (broad s, 1H), 3.0 (broad s, 1H), 5.95 (s, 1H), 7.1 (AA'BB' pattern, 4H, $C_6H_4$).

$C_{17}H_{19}BrO$ (319.25) Calcd. C 63.96 H 6.00 Br 25.03 Found C 64.05 H 6.04 Br 24.97

9. *3',3'-Diphenoxyspiro[adamantane-2,2'-oxetan]-4'-one* (**15**)

a) *From enolate* **12**: To a solution of **12**[12] (3.15 g, 12.3 mmol) in 40 ml of dry THF and 3.0 ml of dry HMPA, kept at −78 °C, was added a solution of adamantanone (2.0 g, 13.3 mmol) in 10 ml of THF. The mixture was stirred under nitrogen for 4 h at −78 °C and for 2 h at 25 °C. After roto-evaporation of the solvent (25 °C/18 Torr), the residue was dissolved in water (80 ml), washed with ether (3 × 30 ml), cooled at 0 °C, acidified slowly with 50% HCl, and extracted with ether (5 × 40 ml). The combined ether extracts were dried over $MgSO_4$ and reto-evaporated (0 °C/18 Torr) almost to dryness. The crude β-hydroxy acid was dissolved in 20 ml of dry pyridine and cooled to 0 °C under nitrogen. Pure benzenesulfonyl chloride (4.15 g, 23.5 mmol) was added dropwise, the mixture stirred at 0 °C for 30 min, and stored overnight in the refrigerator. The dark reaction mixture was poured onto ice-water (50 ml) and extracted with ether (5 × 30 ml). The combined ether extracts were washed with saturated $NaHCO_3$ solution (3 × 20 ml) and with water (5 × 30 ml), dried over $MgSO_4$ and roto-evaporated (25 °C/18 Torr). The residue was submitted to silica gel chromatography (1 : 20 ratio of substrate to adsorbant) at 25 °C, eluting with hexane/ether (4 : 1). Subsequent recrystallization from hexane/ether (4 : 1) gave 1.8 g (40%) of pure **15**, m.p. 105 – 106 °C (plates). – IR ($CCl_4$): 3075, 3050, 2920, 2870, 1830, 1595, 1490, 1460, 1250, 1200, 1170, 1120, 1090, 1050, 1000, 970, 940, 870, 730, 690 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.55 – 2.4 (m, 14H), 6.7 – 7.3 (m, 10H).

$C_{24}H_{24}O_4$ (376.5) Calcd. C 76.57 H 6.43 Found C 76.50 H 6.48

b) *From enolate* **14**: To a cold (−78 °C) LDA-solution (7.81 mmol) in 50 ml of THF was added under nitrogen 1.01 g (3.91 mmol) of methyl diphenoxyacetate. The solution was stirred at −78 °C for 45 min and 1.16 g (7.7 mmol) of adamantanone was added dropwise as 1.5 M solution in THF. The mixture was stirred at −78 °C for 3.5 h and concentrated by roto-evaporation of the solvent (20 °C/18 Torr). The crude mixture was submitted to silica gel chromatography (1 : 20 ratio substrate to adsorbant) at 25 °C, eluting with hexane/ether (4 : 1), resulting in 30 mg (6%) of **15** and 2-adamantyl diphenoxyacetate (**16**) in ca. 14% yield. The latter had the following physical and spectral data: m.p. 98 – 98.5 °C (granular crystals from hexane/ether 3 : 1). – IR ($CCl_4$):

3080, 3050, 2920, 2860, 1750, 1600, 1495, 1455, 1295, 1210, 1130–970, 990, 900, 870, 690 $cm^{-1}$. – NMR ($CCl_4$): δ = 1.5–2.05 (m, 14H, adamantane), 4.85 (broad s, 1H, adamantane), 5.8 (s, 1H, benzhydryl), 6.7–7.25 (m, 10H, PhO).

$C_{24}H_{26}O_4$ (378.5) Calcd. C 76.17 H 6.93 Found C 76.04 H 6.97

10. *(Diphenoxymethylene)adamantane* (**8h**): A solution of **15** (1.8 g, 4.79 mmol) in $CCl_4$ (30 ml) was stirred at 25 °C with silica gel (10 g) for 6–12 h. The silica gel was removed by filtration and washed with 2 × 20 ml of ether. The combined filtrates were roto-evaporated (25 °C/18 Torr) and the residue recrystallized from hexane, affording 1.35 g of pure ketene acetal **8h**, m.p. 95–97 °C (plates). – IR ($CCl_4$): 3080, 3060, 2920, 2860, 1715, 1600, 1500, 1220, 1210, 1160, 1060, 690 $cm^{-1}$. – $^1$H NMR ($CCl_4$): δ = 1.4–2.35 (m, 12H), 2.8 (broad s, 2H), 6.55–7.45 (m, 10H).

$C_{23}H_{24}O_2$ (332.5) Calcd. C 83.10 H 7.28 Found C 82.98 H 7.32

11. *(Morpholinomethylene)adamantane* (**8j**): To a solution of 2-adamantanecarboxaldehyde[31] (7.7 g, 33 mmol) in benzene (120 ml) was added *p*-toluenesulfonic acid (0.50 g, 2.91 mmol) and morpholine (5.0 ml). The mixture was refluxed for 7 h to remove dehydration water by azeotroping. The reaction mixture was washed with water (3 × 40 ml), dried over $MgSO_4$, and roto-evaporated (25–35 °C/18 Torr); subsequent fractional destillation gave 6.5 g (85%) of enamine, b.p. 115 °C/0.2 Torr. It was not possible to obtain a pure sample since the oil would not crystallize. – IR ($CCl_4$): 2910, 2850, 2810, 1670, 1450, 1370, 1270, 1205, 1155, 1120, 1015, 870 $cm^{-1}$. – $^1$H NMR ($CCl_4$): δ = 1.6–2.1 (m, 12H), 2.2 (broad s, 1H), 2.6–2.4 (m, 4H), 2.95 (broad s, 1H), 3.7–3.4 (m, 4H), 5.1 (s, 1H). – $^{13}$C NMR ($CDCl_3$): δ = 27.8, 28.0, 28.1, 28.2, 28.6, 28.8, 29.3, 29.7, 31.4, 32.1, 33.5, 37.0, 37.2, 37.4, 38.0, 38.4, 38.5, 38.7, 38.8, 39.0, 40.0, 40.2, 53.9, 54.0, 56.6, 66.7, 67.0, 67.6, 128.3, 139.4.

$C_{15}H_{23}NO$ (233.4) Calcd. C 77.21 H 9.94 N 6.00 Found C 76.36 H 10.02 N 5.53

12. *[(Phenylthio)methylene]adamantane* (**8k**) was prepared in 62% yield, starting from thioanisole, according to *Corey* and *Seebach*[16] and *Carey* and *Court*[17], m.p. 64–65 °C (granular crystals from ethanol) (lit.[17] 65 °C). – $^{13}$C NMR ($CDCl_3$): δ = 28.5, 34.0, 37.1, 38.8, 39.9, 40.6, 106.5, 125.3, 127.6, 128.8, 138.2, 157.4.

13. *2-Adamantylidene-1,3-dithiane* (**8l**) was prepared in 66% yield, starting from 1,3-dithiane according to lit.[18], m.p. 46–47 °C (granular crystals from pentane) (lit.[18] 45–46 °C). – $^{13}$C NMR ($CDCl_3$): δ = 25.0, 25.7, 26.3, 27.7, 28.4, 29.9, 30.7, 31.5, 34.8, 35.6, 36.8, 38.0, 38.7, 39.3, 102, 154.5.

14. *Dibenzyloxyacetic acid* was prepared in 72% yield, starting from dichloroacetic acid, according to *Fisher* and *Gohlke*[32], m.p. 54–55.5 °C (prisms from hexane/benzene 3:1). – IR ($CCl_4$): 3500–2500, 3080, 3040, 1727, 1500, 1460, 1150–1000, 690 $cm^{-1}$. – $^1$H-NMR ($CCl_4$): δ = 4.45 (s, 4H), 4.85 (s, 1H), 7.05 (s, 10H), 10.8 (s, 1H).

$C_{16}H_{16}O_4$ (272.3) Calcd. C 70.57 H 5.92 Found C 70.46 H 5.96

15. *Methyl dibenzyloxyacetate* was prepared in 89% yield by esterification of dibenzyloxyacetic acid with diazomethane, b.p. 143–145 °C/18 Torr, $n_D^{20}$ = 1.5362. – IR ($CCl_4$): 3080, 3050, 2960, 2890, 1755, 1500, 1460, 1445, 1220, 1150–1000, 730, 695 $cm^{-1}$. – $^1$H NMR ($CCl_4$): δ = 3.6 (s, 3H), 4.5 (s, 4H), 4.82 (s, 1H), 7.1 (s, 10H).

$C_{17}H_{18}O_4$ (286.3) Calcd. C 71.31 H 6.34 Found C 71.42 H 6.39

16. *Methyl α-lithiodibenzyloxyacetate* (**18**): A solution of LDA (0.386 g, 3.61 mmol) in 25 ml of dry THF was cooled to –78 °C and under nitrogen 0.944 g (3.3 mmol) of methyl dibenzyloxyacetate was added in 5 ml dry of THF. The mixture was stirred at –78 °C for 2 h, generating a dark solution. $D_2O$ (2 ml) was added to the enolate solution, the mixture was stirred at 25 °C for

45 min, poured into ice-water (20 ml) and extracted with ether (3 × 15 ml). The combined ether extracts were dried over $MgSO_4$ and roto-evaporated (25 °C/5 – 10 Torr), affording the α-deuterated ester in 50% yield with more than 95% α-deuteration.

17. *Methyl 2,2-dibenzyloxypropionoate:* A sample of 3.3 mmol of **18** solution, prepared by the above procedure, was cooled to −78 °C and 3 ml (excess) of methyl iodide was added. The mixture was allowed to warm up to 25 °C while stirring, washed with water and 10% cold HCl solution (10 ml), dried with $MgSO_4$, and roto-evaporated (29 °C/5 – 10 Torr). The residue was purified by silica gel chromatography (1 : 20 ratio of substrate to adsorbant) at 25 °C, eluting with hexane/ether (1 : 1) and Kugelrohr distillation (170 – 178 °C/0.3 Torr), affording a 90% yield. – IR ($CCl_4$): 3080, 3040, 2960, 1755, 1500, 1460, 1140, 1030, 920, 740, 695 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.54 (s, 3H), 3.6 (s, 3H), 4.42 (s, 4H), 7.1 (s, 10H).

$C_{18}H_{20}O_4$ (300.4) Calcd. C 71.98 H 6.71 Found C 72.01 H 6.75

18. *Methyl 2,2-dibenzyloxy-3-hydroxy-3-methylbutanoate:* To LDA (1.48 g, 13.8 mmol) in dry THF (40 ml, −78 °C) was added a solution of **18** (2.0 g, 6.99 mmol) in THF (5 ml). After stirring at −78 °C for 1.5 h was added 1.1 ml of dry hexamethylphosphoric triamide (HMPA), followed by 5 ml (excess) of acetone after 30 min. The mixture was stirred at −78 °C for 4 to 7 h, allowed to warm up to room temperature and roto-evaporated (28 °C/5 – 10 Torr). The residue was dissolved in 60 ml ether, the solution washed with 30 ml water, dried over $MgSO_4$, roto-evaporated (28 °C/5 – 10 Torr), and submitted to silica gel chromatography (1 : 20 ratio of substrate to adsorbant) at 25 °C, eluting with hexane/ether (3 : 1). 1.20 g (50%) of β-hydroxy-ester was obtained. – IR ($CCl_4$): 3580, 3090, 3070, 3040, 2990, 2950, 2880, 1745, 1500, 1455, 1375, 1345, 1270, 1170 – 1030, 955, 695 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.25 (s, 6H, $CH_3$), 2.45 (s, 1H, OH), 3.65 (s, 3H, $CH_3O$), 4.6 (s, 4H, $CH_2O$), 7.1 (s, 10H, Ph).

$C_{20}H_{24}O_5$ (344.4) Calcd. C 69.91 H 7.11 Found C 69.75 H 7.11

19. *3,3-Dibenzyloxy-4,4-dimethyl-2-oxetanone* (**19**): The above β-hydroxy ester (1.8 g, 5.26 mmol) was stirred with a solution of NaOH (3 g, excess) in $H_2O$ (30 ml) at 90 – 100 °C for 2.5 h. The reaction mixture was allowed to cool to room temperature and washed with ether (1 × 20 ml). After cooling to 0 – 10 °C it was acidified with 20% HCl and extracted with ether (3 × 30 ml). The combined ether extracts were dried over $MgSO_4$ and concentrated by roto-evaporation of the solvent (29 °C/5 – 10 Torr). The residue was dissolved in 8 ml of dry pyridine and cooled to 0 °C. Pure benzenesulfonyl chloride (4.1 g, 23.2 mmol) was added dropwise under nitrogen. The mixture was stirred at 0 °C for 30 min, stored overnight in the refrigerator (ca. 5 °C), then poured onto 30 ml ice-water, and extracted with ether (3 × 30 ml). The combined ether extracts were washed with saturated $NaHCO_3$ solution (3 × 20 ml) and water (4 × 20 ml), dried over $MgSO_4$, and roto-evaporated (28 °C/5 – 10 Torr). The residue was submitted to silica gel chromatography (1 : 30 ratio of substrate to adsorbant) at 25 °C, eluting with hexane/ether (4 : 1), affording 0.60 g (37%) of pure **19** as viscous oil. – IR ($CCl_4$): 3095, 3080, 3040, 2990, 2940, 2890, 1835, 1500, 1460, 1390, 1385, 1285, 1175, 1115, 1085, 830 – 710, 695 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.46 (s, 6H, $CH_3$), AB pattern at $\delta_A$ = 4.40 and $\delta_B$ = 4.63 ($J$ = 12 Hz, 4H, $CH_2O$), 7.06 (broad s, 10H, Ph).

$C_{19}H_{20}O_4$ (312.4) Calcd. C 73.06 H 6.45 Found C 73.18 H 6.50

20. *3',3'-Dibenzyloxyspiro[adamantane-2,2'-oxetan]-4'-one* (**20**) *and 2-adamantyl dibenzyloxyacetate* (**21**): To a solution of LDA (0.75 g, 6.99 mmol) in 40 ml THF at −78 °C was added methyl dibenzyloxyacetate (1.0 g, 3.49 mmol), dissolved with dry THF (5 ml). The mixture was stirred at −78 °C for 1.5 h and HMPA (1.1 ml) was added. After an additional 0.5 h stirring at −78 °C, adamantanone (1.5 g, 7.0 mmol) was added, contained in 5 ml of dry THF. The reaction mixture was stirred at −78 °C for 4 h and immediately roto-evaporated (25 °C/18 Torr). The residue was dissolved in 70 ml ether, the solution washed with 25 ml water, and dried over $MgSO_4$. After roto-

evaporation of the solvent (28 °C/18 – 20 Torr), the residue was submitted to silica gel chromatography (1 : 20 ratio of substrate to adsorbant), eluting with hexane/ether (4 : 1), affording 50 mg (3.5%)[33] of β-lactone **20** and 100 mg (18%) of ester **21**.

*2-Oxetanone* **20**: m.p. 105 – 106 °C (plates from hexane/ether). – IR ($CCl_4$): 3095, 3080, 3040, 2920, 2870, 1820, 1500, 1460, 1180, 1140, 1130, 1120, 1100, 1060, 870, 850, 730, 695 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.55 – 2.15 (m, 14H, adamantane), 4.75 (s, 4H, $CH_2O$), 7.05 (s, 10H).

$C_{26}H_{28}O_4$ (404.5) Calcd. C 77.20 H 6.98 Found C 77.17 H 7.02

*Ester* **21**: m.p. 62 – 64 °C (granular crystals from hexane/ether). – IR ($CCl_4$): 3100, 3080, 3050, 2920, 2870, 1749, 1500, 1460, 1290, 1215, 1150 – 980, 730, 690 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.5 – 2.2 (m, 14H ad), 4.53 (s, 4H, $CH_2O$), 4.8 (m, 1H, OCH), 4.85 [s, 1H, $CH(OR)_2$], 7.11 (s, 10H).

$C_{26}H_{30}O_4$ (406.5) Calcd. C 76.82 H 7.44 Found C 76.76 H 7.47

21. *General Procedure for Dioxetanes* **9e, f,** *and* **g**: About 1.0 mmol of the enol ether was dissolved in 5 ml of $CCl_4$; after addition of polymer-bound Rose Bengal (10 mg) the solution was cooled to 0 °C and irradiated with a 150 W sodium street lamp under a constant oxygen flow. After complete reaction, as monitored by $^1H$ NMR, the sensitizer was removed by filtration and washed with 10 ml $CH_2Cl_2$. The filtrate and wash were concentrated by roto-evaporation (0 °C/5 – 10 Torr). The yellow residue was recrystallized from pentane, affording the dioxetane in 25 to 42% yield. The details for the individual dioxetanes are given below.

22. *4'-Phenoxyspiro[adamantane-2,3'-[1,2]dioxetane]* (**9e**): 25% yield, m.p. 85 – 87.5 °C (prisms from pentane). – IR ($CCl_4$): 3050, 2920, 2860, 1595, 1495, 1455, 1220, 1110, 1095, 1060, 1015, 960, 865, 740, 690 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.6 – 2.9 (m, 14H), 5.8 (s, 1H), 6.6 – 7.3 (m, 5H).

$C_{17}H_{20}O_3$ (272.2) Calcd. C 74.96 H 7.41 Found C 75.00 H 7.42

23. *4'-(4-Bromophenoxy)spiro[adamantane-2,3'-[1,2]dioxetane]* (**9f**): 25% yield, m.p. 85 – 87.5 °C (prisms from pentane). – IR ($CCl_4$): 2920, 2870, 1490, 1460, 1370, 1230, 1110, 1095, 1075, 1060, 1015, 915, 890 – 720 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.5 – 2.8 (m, 14H), 5.7 (s, 1H), 7.0 (AA'BB' pattern, 4H, $C_6H_4$).

$C_{17}H_{19}BrO_3$ (351.3) Calcd. C 58.13 H 5.45 Br 22.75 Found C 58.30 H 5.48 Br 22.61

24. *4'-Benzyloxyspiro[adamantane-2,3'-[1,2]dioxetane]* (**9g**): 23% yield, m.p. 76 – 77.5 °C (prisms from pentane). – IR ($CCl_4$): 3095, 3060, 3035, 2920, 2860, 1500, 1450, 1360, 1160, 1145, 1130, 1100, 1060, 1005, 950, 935, 730, 690 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 1.5 – 2.9 (m, 14H), AB pattern at $\delta_A$ = 4.45, $\delta_B$ = 4.78 ($J$ = 12 Hz, 2H, $CH_2O$), 5.45 (s, 1H), 7.2 (s, 5H).

$C_{18}H_{22}O_3$ (286.2) Calcd. C 75.48 H 7.75 Found C 75.28 H 7.82

25. *General procedure for the synthesis of dioxetanes* **9c** *and* **h**: A solution of 0.67 mmol of the appropriate olefin and ca. 3 mg of tetraphenylporphyrin in 6 ml of $CH_2Cl_2$ was cooled at –20 °C and then irradiated for 6 – 8 h with a 150 W sodium street lamp under a constant oxygen flow. The reaction mixture was concentrated to a volume of ca. 2 ml by roto-evaporation (0 °C/18 Torr) and the concentrate was submitted to Florisil chromatography (1 : 40 ratio of substrate to adsorbant) at –40 °C, eluting with $CH_2Cl_2$. Recrystallization from pentane/$CH_2Cl_2$ gave the pure product. The details for the individual dioxetanes are described below.

26. *Dispiro[adamantane-2,3'-[1,2]dioxetane-4',9''-fluorene]* (**9c**): 70% yield. The reaction progress was monitored by $^1H$ NMR; m.p. 105 – 107 °C (prisms from pentane/ether). – IR ($CCl_4$): 3075, 2925, 2865, 1615, 1455, 1275, 1225, 1080, 1045, 990, 735, 680 $cm^{-1}$. – $^1H$ NMR ($CCl_4$): δ = 0.4 – 2.2 (m, 12H, adamantane), 2.9 (broad s, 2H, adamantane), 6.9 – 7.5 (m, 6H, aromatic),

7.8 (m, 2H, aromatic). – $^{13}$C NMR ($CDCl_3$): δ = 25.5, 27.5, 31.9, 33.3, 33.7, 36.1, 36.4, 39.3, 47.0, 94.5, 97.7, 120.1, 120.3, 124.2, 126.8, 127.2, 129.1, 130.2, 134.6, 140.1, 142.8.

$C_{23}H_{22}O_2$ (340.3) Calcd. C 83.60 H 6.71 Found C 83.71 H 7.09

27. *4',4'-Diphenoxyspiro[adamantane-2,3'-[1,2]dioxetane]* (**9h**): 89% yield. The reaction progress was monitored by IR; m.p. 103.5 – 105 °C (prisms from pentane/$CH_2Cl_2$). – IR ($CCl_4$): 3080, 3050, 2920, 2870, 1600, 1495, 1455, 1335, 1290, 1265, 1225, 1200, 1165, 1120, 1050, 1000, 910, 870, 695 cm$^{-1}$. – $^1$H NMR ($CCl_4$): δ = 1.5 – 2.2 (m, 12H), 2.8 (m, 2H), 6.7 – 7.1 (m, 10H). – $^{13}$C NMR ($CDCl_3$): δ = 25.9, 26.0, 26.6, 31.4, 32.1, 32.5, 32.7, 33.2, 34.4, 35.0, 35.7, 37.1, 117.8, 120.7, 121.9, 123.6, 124.9, 128.5, 128.6, 129.8, 152.6, 152.7.

$C_{23}H_{24}O_4$ (364.5) Calcd. C 75.80 H 6.64 Found C 75.92 H 6.56

28. *3'-Phenylspiro[adamantane-2,4'-[5,6,11,12]tetraoxatricyclo[6.2.2.0$^{2,7}$]dodeca-2,9-diene]* (**23**): A solution of **8b** (0.606 g, 2.02 mmol) and tetraphenylporphyrin (ca. 5 mg) in $CH_2Cl_2$ (8 ml) was cooled to –40 °C and then irradiated with a 150 W sodium street lamp while passing oxygen gas for 24 h. The reaction mixture, which still contained some starting material, was submitted to Florisil chromatography (1 : 40 ratio of substrate to adsorbant) at –40 °C, eluting with $CH_2Cl_2$, affording **23** (460 mg, 73%) m.p. 116 – 118 °C (needles from $CH_2Cl_2$/pentane/ether). – IR ($CCl_4$): 3080, 3020, 2980, 2900, 2860, 1600, 1495, 1470, 1450, 1360, 1110, 920, 900, 695 cm$^{-1}$. – $^1$H NMR ($CCl_4$): δ = 1.2 – 2.8 (m, 14H), 4.2 (m, 1H), 4.45 (s, 1H), 4.5 – 4.7 (m, 1H), 6.3 (m, 2H), 6.7 – 7.3 (m, 5H).

$C_{23}H_{24}O_4$ (364.5) Calcd. C 75.80 H 6.63 Found C 75.89 H 6.58

29. *2-Hydroperoxy-2-isopropenyladamantane* (**24**): A solution of **8d** (0.75 g, 4.26 mmol) and tetraphenylporphyrin (3 mg) in $CH_2Cl_2$ (10 ml) was cooled to –78 °C and then irradiated with 150 W sodium street lamp while passing oxygen gas for 4 h. After complete reaction, as monitored by $^1$H NMR, the reaction mixture was concentrated to ca. 2 ml and submitted to Florisil chromatography (1 : 30 ratio of substrate to adsorbant) at –30 °C, eluting with $CH_2Cl_2$. 750 mg of pure **24** was isolated, m.p. 65 – 67 °C (needles from pentane/$CH_2Cl_2$). – IR ($CCl_4$): 3500, 3095, 2920, 2860, 1640, 1460, 1450, 1380, 1370, 1340, 1100, 1070, 1060, 1015, 980, 915 cm$^{-1}$. – $^1$H NMR ($CCl_4$): δ = 1.4 – 2.4 (m, 14H), 1.7 (s, 3H), 5.55 (broad s, 1H), 5.7 (m, 1H), 6.8 (s, 1H).

$C_{13}H_{20}O_2$ (208.3) Calcd. C 74.96 H 9.68 Found C 75.20 H 9.81

30. *4'-(Bromomethyl)-4'-methylspiro[adamantane-2,3'-[1,2]dioxetane]* (**26**): A mixture of mercury trifluoroacetate (2.2 g, 5.16 mmol) and $CH_2Cl_2$ (40 ml) was cooled to –40 °C and **24** (1.06 g, 5.09 mmol) was added at once and the mixture stirred magnetically at –40 °C for 2.5 h. The yellow solution was then warmed up to –20 °C and a solution of bromine (1 ml) in $CH_2Cl_2$ (15 ml) was added dropwise until the bromine color persisted. After stirring for 10 min at –20 °C, the reaction mixture was washed with cold water (4 × 20 ml), with saturated aqu. $Na_2CO_3$ solution (2 × 25 ml), and with 30 ml of cold water again. The slightly yellow organic phase was dried over $MgSO_4$ and the solvent removed by roto-evaporation (3 °C/18 Torr), affording a yellow oil which was submitted to silica gel chromatography (1 : 30 ratio of substrate to adsorbant) at –39 °C with $CH_2Cl_2$ as elevant. 450 mg (29%) of pure product were isolated, m.p. 108 – 110 °C (prisms from pentane/$CH_2Cl_2$). – IR ($CCl_4$): 2920, 2860, 1460, 1385, 1240, 1105, 1095, 1090, 1060, 1005, 920, 865 cm$^{-1}$. – $^1$H NMR ($CCl_4$): δ = 1.5 (s, 3H), 1.7 (broad s, 12H), 2.3 – 2.8 (m, 2H), 3.7 (s, 2H). – $^{13}$C NMR ($CDCl_3$): δ = 18.8, 25.0, 25.4, 28.7, 30.3, 30.7, 31.2, 31.5, 31.9, 32.00, 32.2, 33.5, 33.8, 34.2, 35.4, 88.1, 92.6.

$C_{13}H_{19}BrO_2$ (287.2) Calcd. C 54.37 H 6.67 Found C 54.50 H 6.71

31. *General procedure for the synthesis of dioxetanes* **9k** *and* **l**: About 1.34 mmol of the appropriate olefin was dissolved in $CDCl_3$ (ca. 6 ml), polymer-bound Rose Bengal (ca. 100 mg) was

added, the suspension cooled to −70 °C, and irradiated with a 150 W sodium street lamp under a constant oxygen flow. The reaction progress was followed by $^1$H NMR ($CDCl_2$). After complete reaction the polymer-bound Rose Bengal was removed by filtration at −75 °C and the filtrate submitted to $^1$H NMR ($CDCl_3$) at −30 to −50 °C. Additionally the singlet oxygenation was carried out with tetraphenylporphyrin as sensitizer directly in an NMR tube and analyzed by $^{13}$C NMR ($CDCl_3$) at −60 to −70 °C.

32. *4'-(Phenylthio)spiro[adamantane-2,3'-[1,2]dioxetane]* (**9k**) could not be isolated and purified. – $^1$H NMR ($CDCl_3$) at −30 °C: δ = 1.4–2.3 (m, 12H), 2.66 (broad s, 2H), 6.16 (s, 1H), 7.1 (m, 5H). – $^{13}$C NMR ($CDCl_3$) at −63 °C: δ = 25.5, 30.3, 31.4, 32.9, 33.3, 34.2, 35.3, 36.9, 38.9, 93.1, 100.2, 127.9, 129.1, 131.5, 133.0, 215.5, 225.8, 229.4.

33. *Dispiro[adamantane-2,3'-[1,2]dioxetane-4',2''-[1,3]dithiane]* (**9l**) could not be isolated and purified. – $^1$H NMR ($CDCl_3$) at −50 °C: δ = 1.45–2.3 (m, 14H), 2.74–3.12 (m, 4H), 3.32–3.5 (m, 2H). – $^{13}$C NMR ($CDCl_3$) at −60 °C: δ = 21.2, 21.8, 22.4, 24.6, 25.1, 25.2, 25.4, 25.7, 25.8, 26.1, 30.8, 31.4, 31.9, 32.9, 33.5, 34.0, 34.6, 35.0, 35.6, 36.1, 38.8, 96.6, 109.6.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[33] A shorter reaction time (2 h) increased the β-lactone yield to 25%.

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